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Apparatus for producing hydrogen

The present invention relates to an apparatus for producing hydrogen according to the preamble of Claim 1.

An apparatus of the type cited at the beginning is described in the previously published DE 202 11 546 U1 and the subsequently published DE 102 40 953 A1 and EP 1 415 705 A1. This apparatus comprises, inter alia, a steam reformer stage, preferably heatable using a burner, for converting hydrocarbon gas and water into hydrogen and further reformer products such as carbon dioxide and carbon monoxide. For example, a PEM fuel cell may be operated using the hydrogen produced. Since the reformat still contains a comparatively large amount of carbon monoxide after the reformer stage (fuel-cell poison), a catalyst stage is connected downstream therefrom, in order to catalytically convert the carbon monoxide into carbon dioxide (unproblematic for the fuel cell). For ultrapurification, i.e., to reduce the carbon monoxide content in the reformat even further, finally a methanization stage is connected downstream from the catalyst stage, which converts the remaining carbon monoxide (back) into methane gas using hydrogen. The entry temperature of the reformat gas containing the carbon monoxide into the methanization stage is typically approximately 240°C in this case. Since the methanization process proceeds exothermically, cooling of the methanization stage is necessary. For this purpose, a flow guiding housing for a coolant is provided, which is assigned to the stage alternately externally or from the interior (for hollow-cylindrical implementation, for example), depending on the implementation of the methanization stage. This flow guiding housing may have the coolant

flow through it in parallel flow or counterflow to the reformat flow as needed.

Experiments have now shown that the reformat gas at the outlet of the methanization stage, in spite of the cooling described using a coolant guided through the flow guiding housing, has an unexpectedly high carbon monoxide content (100 ppm and more), which is unacceptable, since the carbon monoxide - as noted - is harmful to the fuel cell. The cause for this high carbon monoxide content is apparently a retroshift reaction, in which the hydrogen just produced reacts with the reformer product carbon dioxide and forms carbon monoxide and water. This reaction is undesired because of the consumption of the hydrogen just produced, and in addition because of the harmful effect of the carbon monoxide on the fuel cell mentioned.

The present invention is accordingly based on the object of ensuring in the simplest possible way, in an apparatus of the type cited at the beginning, that this retroshift reaction does not occur and the carbon monoxide component in the reformat gas at the outlet of the methanization stage is as low as possible, preferably significantly less than 100 ppm.

This object is achieved with an apparatus of the type cited in the beginning by the features listed in the characterizing part of Claim 1.

It is accordingly provided according to the present invention that the flow guiding housing has at least two, preferably three or more cooling zones having different cooling effects situated one behind another in the axial direction. The use of at least two cooling zones results in a stepped or

continuously changing temperature curve within the methanization stage - depending on the constructive implementation of the cooling zones - which in turn results, with corresponding coolant temperature, in the temperature being reduced significantly toward the exit of the methanization stage in spite of the exothermic methanization process and the undesired retroshift reaction accordingly not occurring. The special advantage of the present invention is thus that the temperature curve within the methanization stage may be influenced in a targeted way and a minimal carbon monoxide content in the reformat gas may be achieved in this way.

Thanks to the achievement of the object according to the present invention, an "air bleed" may also be dispensed with in this case, which until now was connected downstream from the methanization stage and upstream from the fuel cell, and in which the residual carbon monoxide contained in the reformat was oxidized using small quantities of oxygen.

For the sake of completeness, reference is additionally made to US 3,441,393 A, from which a method for producing a hydrogen-rich gas is known. In this facility, a "commercially available" methanization stage is provided, i. e., not a gas ultrapurification stage having the multizone cooling according to the present invention. With this achievement of the object, the reformat gas enters the methanization reactor at 316°C and leaves it at 379°C, i. e., even heated by 63°C. The recognition according to the present invention of cooling the methanization stage in multiple stages in order to prevent a retroshift reaction cannot be inferred from this publication.

Other advantageous refinements of the present invention result from the dependent claims.

The apparatus according to the present invention, including its advantageous refinements, is explained in greater detail in the following on the basis of the drawing of different exemplary embodiments using multiple diagrams.

Figure 1 schematically shows the apparatus according to the present invention having a methanization stage having four cooling zones in section;

Figure 2 shows the temperature curve as a diagram plotted over the run length x within the methanization stage when one cooling zone is used (related art);

Figure 3 shows the temperature curve as a diagram plotted over the run length x within the methanization stage when four cooling zones are used;

Figure 4 shows the temperature curve as a diagram plotted over the run length x within the four cooling zones;

Figure 5 schematically shows two further embodiments of the flow guiding housing on the methanization stage in section (summarized in one illustration for the sake of simplicity); and

Figure 6 schematically shows a further embodiment of the flow guiding housing on the methanization stage in section.

Figure 1 schematically shows the apparatus according to the present invention for producing hydrogen in section.

This comprises a reformer stage 1 for converting hydrocarbon gas and water into hydrogen and further reformer products. The reformer stage 1, which has a reformer catalyst, is preferably implemented, as shown, as a steam reformer stage

heated using a burner 9, in particular a gas burner, i.e., in this stage, for example, CH_4 and H_2O are converted into CO , CO_2 , and H_2 while heat is supplied (by the burner 9) (endothermic reaction). In order to ensure the most uniform possible temperature curve within the reformer stage 1 and thus optimum hydrogen production, the reformer stage 1 is preferably implemented as a hollow cylinder, as shown.

Furthermore, the apparatus according to the present invention comprises at least one catalyst stage 2, connected downstream from the reformer stage 1, for catalytic conversion of the carbon monoxide, i. e., this is at least partially converted into carbon dioxide, which is harmless to the fuel cell. As in the reformer stage 1, the catalyst stage 2 is advantageously also implemented as a hollow cylinder. This measure results in a more uniform temperature curve and thus in better carbon monoxide conversion within the catalyst stage 2.

Finally, the apparatus according to the present invention comprises a methanization stage 3 connected downstream from the catalyst stage 2, which has axial flow through it and which, as noted, is used for the purpose of methanizing as much as possible of the residual carbon monoxide contained in the reformat gas using hydrogen. For temperature control of the methanization stage 3, a flow guiding housing 4 for a coolant, which extends in the axial flow direction, is assigned thereto. The methanization stage 3 is preferably also implemented as a hollow cylinder, as shown.

In order to ensure flow through the individual stages of the apparatus according to the present invention which is as free

of pressure loss as possible, it is also advantageously provided that the reformer stage 1, the catalyst stage 2, and the methanization stage 3 are situated one after another in the axial flow direction. With a hollow-cylindrical implementation, is also advantageous for the stages to be situated one after another defining a continuous annular chamber in the axial flow direction.

It is essential for the apparatus according to the present invention for producing hydrogen that the flow guiding housing 4 has at least two, preferably three or more cooling zones 5, 6, 7, 8 having different cooling effects situated one after another in the axial direction.

In the embodiment shown in Figure 1, the flow guiding housing 4 is divided into four cooling zones 5, 6, 7, 8, to each of which the coolant may be supplied separately. In principle, however, two zones are already capable of achieving the object defined at the beginning. The more cooling zones are provided, the more precisely may the temperature curve within the methanization stage be fixed, but the outlay for apparatus also becomes greater. Four zones have been shown to be a favorable selection here.

With a hollow-cylindrical implementation of the methanization stage 3, it has also been shown to be advantageous for the cooling zones 5, 6, 7, 8 to be situated alternately inside and/or outside the methanization stage 3 (see Figure 6). In this case, the cooling zones 5, 6, 7, 8 preferably enclose the methanization stage 3 like annular chambers situated axially one after another or, with a hollow-cylindrical implementation of the methanization stage 3, are enclosed thereby (see Figure 6 again).

As schematically shown in Figure 1, it is also advantageous for each cooling zone 5, 6, 7, 8 to have at least one coolant supply connection 10 and one coolant removal connection 11, each cooling zone 5, 6, 7, 8 additionally advantageously being able to have coolant flow through it alternately in parallel flow (not shown) or in counterflow to the methanization stage 3.

In order to also implement optimum cooling which is adapted to the requirements, it is advantageous for different coolants to be supplied to the cooling zones 5, 6, 7, 8.

Furthermore, it is advantageous for a coolant which is used to be supplied alternately at different temperatures to the individual zones 5, 6, 7, 8 or, if different coolants are used, for these to have different temperatures, for example, by using heat exchangers (not shown).

Figure 2 shows a temperature curve over the run length x (see Figure 1) within a methanization stage, which only has one cooling zone (related art). As noted, carbon monoxide and hydrogen is converted back into hydrocarbon gas (methane) in the methanization stage in order to reduce the carbon monoxide component in the reformat gas. Since the methanization is an exothermic procedure, the temperature first rises in the stage and then falls because of the cooling to a value just below the entry temperature. With a construction of this type, the carbon monoxide content is typically approximately 120 ppm, i.e., too much to conduct the reformat gas directly to the fuel cell. As noted, an "air bleed" is therefore typically connected downstream from

the methanization stage in order to also remove this component of carbon monoxide.

The cause for the still comparatively high carbon monoxide component in the reformat gas after the methanization stage has been shown to be that retroshift reactions, in which carbon dioxide and hydrogen react to form carbon monoxide and water, occur again and again because of the quite high temperatures at the outlet of the stage.

According to the present invention, as described, the methanization stage is divided into multiple cooling zones in order to lower the temperature toward the outlet of the stage in a targeted way so that the undesired retroshift reactions no longer occur. A corresponding temperature curve is shown in Figure 3, which may be implemented if the cooling zone distribution according to the present invention is used. The temperature in the methanization stage thus falls with this achievement of the object continuously from 240°C to approximately 220°C, with the result that, in particular at the end of the methanization stage, retroshift reactions may no longer occur, since the temperatures are too low for this purpose in the area of this cooling zone. The reference numbers 5, 6, 7, 8 and the dotted lines in Figure 3 are to illustrate the area where the cooling zones are situated.

Figure 4 illustrates the temperature curve within the individual cooling zones. It is particularly noticeable that because of the cooling in counterflow, a type of sawtooth profile arises, but the temperature peaks always fall again toward the outlet of the stage, from which the desired, falling temperature curve within the methanization stage may necessarily be concluded.

According to the two further embodiments of the flow guiding housing 4 of the methanization stage illustrated in Figure 5, it is provided as alternative to the achievement of the object shown in Figure 1 that the cooling zones 5, 6, 7, 8 situated one behind another in the axial direction are directly hydraulically connected to one another, but have different flow cross-sections. According to the present invention, a direct hydraulic separation of the cooling zones 5, 6, 7, 8 is not required, rather the heat transmission in the individual areas of the methanization stage may also be influenced in a targeted way through suitable selection of the axial flow cross-sections. In this case, a large flow cross-section means a low flow speed and therefore relatively poor heat transmission, or a small cross-section means a high flow speed and therefore quite good heat transmission; all also as a function of temperature gradient between coolant and methanization stage, of course.

Finally, it is advantageously provided according to the upper illustration in Figure 5 that the cooling zones 5, 6, 7, 8 have stepped flow cross-sections to one another in the axial direction. Alternatively (lower illustration) continuously changing flow cross-sections are also provided, in both cases the cooling zones 5, 6, 7, 8 alternately being able to have coolant flow through them in parallel flow or counterflow to the methanization stage 3.

List of reference numbers

- 1 reformer stage
- 2 catalyst stage
- 3 methanization stage
- 4 flow guiding housing
- 5 cooling zone
- 6 cooling zone
- 7 cooling zone
- 8 cooling zone
- 9 burner
- 10 coolant supply connection
- 11 coolant removal connection